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OCCURRENCE AND FORMATION OF N-DBPS IN

RHODE ISLAND DRINKING WATERS

BY

MAXWELL C. MEADOWS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

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IN

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2019

MASTER OF SCIENCE THESIS

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ABSTRACT

N-nitrosamines are toxic compounds that have persistently been associated with water treatment processes since the 1970's. There are currently no federal regulations for N-nitrosamines in drinking water, however few states have established their own guidelines. Many studies have identified major mechanisms of N-nitrosamine formation during water treatment, however a gap in knowledge still exists regarding the formation of select N-nitrosamines from treatment of clean water sources. Performance of such critical research is often an expensive process, leaving many facilities and institutions resorting to other approaches for analysis. In the case of this research, efforts were made to develop a lower-cost, and widely applicable method for N-nitrosamine analysis utilizing standard liquid-liquid extraction techniques, coupled with common GC-MS analytics. This study also focused on identifying the formation potential of select N-nitrosamines during treatment of seasonally and spatially varying source water, using a bench-top water treatment system. Results from the method development section show that the method was capable of detecting 9 target N-nitrosamines at a concentration of 2 µg/L, suggesting that this method could be applied to N-nitrosamine formation pathway studies. To perform N-nitrosamine analysis in the water treatment study, a lower limit of detection was required, therefore analysis was outsourced to a laboratory at Kagoshima University,

Japan. Results from the water treatment section show that the system design did not reduce the likelihood of forming select N-nitrosamines during pre-treatment, and the formation of those N-nitrosamines was significantly dependent on factors such as disinfection contact time, precursors, and source water type. All results from this research will supplement the science of previous N-nitrosamine studies, and promote future N-nitrosamine research as it relates to water treatment.

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To my family, my partner Mary, and all my friends back home, thank you for your constant love and support, for I could not have gone this far without it. This thesis is dedicated to my best friend Cory Francks. I love you brother.

PREFACE

This thesis is written in manuscript format. Chapter 1 was published in MATEC Web of Conferences. Chapter 2 was formatted for submission to Chemosphere. Chapter 3 was formatted for submission to Water.

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CHAPTER 1

Chapter 1 has been formatted to the MATEC Web of Conferences publication guidelines.

Nitrosamines: A review of formation pathways, precursors, control, and occurrence in drinking water

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Abstract. Nitrogenous disinfection by-products (N-DBPs) are emerging by-products that may be present in drinking water as by-products of water treatment plant (WTP) operations. Nitrosamines are N-DBPs that form by reaction of chloramine with certain organic nitrogen-containing compounds; however, the exact processes and environments in which nitrosamines form are still not well understood. Organic nitrogen precursors react within the WTP and distribution system, forming the toxic by-products during chloramination, or while in distribution. To best control the formation potential of nitrosamines, precursors must be removed from source water prior to chloramine disinfection. These nitrosamine forming precursors are abundant in source waters worldwide, presenting a need for further study of the mechanisms that reduce the formation potential of nitrosamines in chloramination WTPs.

1 Introduction

Nitrogenous disinfection byproducts (N-DBPs) are toxic pollutants of emerging concern that may be present in source waters from industrial or wastewater discharge, septic systems, or as byproducts of water treatment plant (WTP) operations. Specifically, N-DBPs such as nitrosamines can form by the reaction of precursors within a treatment plant or chloraminated distribution system [1, 2]. Many nitrosamines that have been studied are classified as probable carcinogens, as indicated by the U.S. Environmental Protection Agency's

(USEPA's) Integrated Risk Information System (IRIS) database. [1, 3] documented the reactions of chloramines with organic nitrogen precursors as the primary mechanism responsible for N-DBP formation in WTPs. These precursors to nitrosamine formation are abundant in many global drinking water sources and can be formed in the distribution systems, making these supplies particularly susceptible to nitrosamine formation. This review provides an assessment of formation pathways and precursors of nitrosamines, mechanisms for control of nitrosamine formation, and the global occurrence of nitrosamines in drinking water.

2 Nitrosamine formation in drinking water: chloramination

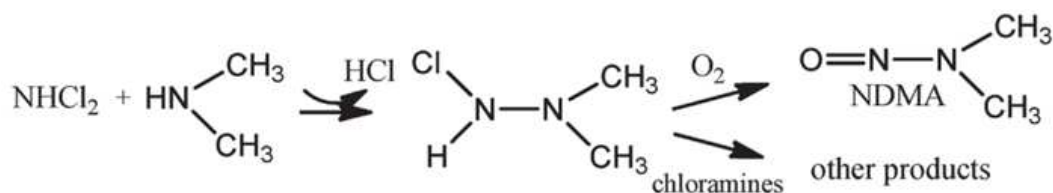
Drinking water treatment is a major pathway to nitrosamine formation. Previous studies have documented nitrosamine formation from several mechanisms of WTP operations, including chloramination, ozonation, and chlorine-nitrite interaction [2]. The degree of influence on formation of nitrosamines varies between all WTP processes.

Chloramine disinfection is the most important pathway for nitrosamine formation [4]. Findings from [3, 5] showed nitrosamine formation occurred by reaction of monochloramine and amine precursors. [1] later explained that both monochloramine (NH_2Cl) and dichloramine (NHCl_2) coexist under typical

chloramine disinfection conditions, and both are responsible for nearly all nitrosamine formation in drinking water treatment:



[4] demonstrated the formation of N-nitrosodimethylamine (NDMA) and other nitrosamines from reactions that occur during chloramination (Scheme 1). A nucleophilic substitution reaction between dimethylamine and NHCl_2 forms a chlorinated unsymmetrical dimethylhydrazine intermediate (CI-UDMH). Oxidation of CI-UDMH by dissolved oxygen forms NDMA and other nitrosamines. This particular formation pathway has a slow reaction process, often days, indicating that nitrosamines continue formation and accumulation within a chloraminated distribution system [6, 7].



Scheme 1 – From [4].

3 Nitrosamine precursors in source waters

Source waters utilized for consumption are extremely influential to nitrosamine formation potential. Quality of source water is largely dependent on factors such as watershed and source water type. Seasonal variation is also known to have significant impact on disinfection byproducts [8]. Through proper assessment of source water before disinfection, WTPs can provide potable water while preventing the formation of nitrosamines.

Evaluation of nitrosamine formation potential begins with proper source water assessment. Watershed variation generates differences in precursor type and relating concentrations. Amines are expected to be the major nitrosamine forming precursor during chloramination [2]. Although the reaction time is much slower, amides are the other major category of organic nitrogen precursors [9].

Signatures of amine and amide precursors exist multiple watershed types, including urban and agricultural. Source water containing high concentrations of precursors is likely impaired by treated wastewater, industrial effluents, or herbicides diuron and dimethyldithiocarbamate [9-13].

Surface runoff enriched with heavy metals, nutrients and sediments, rubber fragments, and other contaminants is an essential source of non-point source pollution to receiving water bodies such as drinking water reservoirs [14, 15]. Forested watersheds naturally offer more protection to source water, rather

than urban or agricultural watersheds. Forested buffers located around a reservoir system limit the direct influence of contaminated runoff on quality of source water. Buffer areas change the quantity of water available for runoff through interception, evapotranspiration, infiltration, percolation, and absorption, resulting in different physical, chemical, and biological processes in the receiving water bodies [14].

4 Control of nitrosamine formation

Removal of nitrosamines following drinking water treatment is a difficult task, as many nitrosamines are hydrophilic ($\log K_{ow} = -0.57$ for NDMA), and will poorly sorb to activated carbon, and other sorbents [7, 16]. NDMA has a relatively high vapor pressure at 2.7 mm Hg at 20°C [17]. The estimated Henry's Law constant for NDMA is low at 2.6×10^{-7} atm-m³/mol at 20°C, due to the high water solubility of NDMA [16, 18]. Due to the chemical and physical properties of NDMA, volatilization from air stripping during water treatment is unlikely to result in significant removal from solution [7].

Removal of nitrosamine precursors before disinfection is a vital process to control nitrosamine formation during drinking water treatment. Furthermore, nitrosamines will typically not be present in drinking waters treated by activated carbon prior to chloramination [2]. Sorption of precursors exposed to powdered activated carbon (PAC) at a dose of 5 mg/L for 7 days, showed 50% reduction of

NDMA formation potential [19]. During the same study, water exposed to a PAC dose of 20 mg/L for 7 days produced an NDMA formation potential reduction of 90%. Water was in contact with PAC for 7 days to assure establishment of adsorption equilibrium, even though conventional treatment contact times typically last hours [19].

A study conducted by [20] demonstrated that by using granular activated carbon (GAC) to treat a mixture of 90% surface water and 10% wastewater at a 10-minute simulated empty bed contact time, NDMA formation potential breakthrough was less than 20% after 10,000 bed volumes. Also, GAC demonstrated 60-80% reduction of NDMA formation potential in surface waters during pilot- and full-scale studies [20].

5 Global occurrence of nitrosamines

The presence of nitrosamines is worldwide and relatively similar among all detection locations. Given the expectations from known formation pathways, North American studies found that NDMA formation is closely associated with chloramination than with chlorination [15, 21-23]. Water treatment plants with long disinfection chloramine contact times (12-18 hours) tended to have greater NDMA concentrations in the plant effluent than those with short (0.5-2 hours) contact times, due to the long time-scales of nitrosamine formation [24]. One large study collected drinking water samples under the second Unregulated

Contaminants Monitoring Rule (UCMR2). NDMA was detected in 34% of chloramination plant effluents [23]. Other nitrosamines N-nitrosodiethylamine (NDEA), N-nitrosopyrrolidine (NPYR), N-nitrosodi-n-butylamine (NDBA), and N-nitrosomethylethylamine (NMEA) were also detected, but each at less than 1% occurrence [23].

[25] performed a nitrosamine occurrence study in England and Wales. Out of 41 surveyed plants, only 3 had detectable concentrations of NDMA; however, the levels were always below 6 ng/L. Another UK study conducted by [26] found NDMA concentrations just above the method detection limit (0.9 ng/L) in a few isolated samples from one distribution system. WTP practices in the UK typically operate with a set 30 minute pre-chlorine contact time, and low chloramine disinfection dose (0.5 mg/L), explaining why such low NDMA concentrations are found in chloraminated drinking waters of the UK [26].

High nitrosamine occurrence was seen in Australia due to the high prevalence of chloramination WTPs. One study detected NDMA in 75% of chloraminated waters, where 37% of the detections had NDMA concentrations >10 ng/L [27]. Besides the high rate of chloramination WTPs, wastewater recycling, and high source water ammonia concentrations are accountable for such high levels of NDMA in drinking water in Australia [27, 28].

The occurrence of nitrosamines in China can be explained by circumstances other than drinking water treatment practices. In recent surveys of Chinese waters, nitrosamines frequently occurred due to impairment from domestic and industrial wastewaters [29, 30]. Due to the influence of industrial and domestic wastewaters, nitrosamines other than NDMA such as NPYR, NMOR, and NPIP, were detected more frequently in China than in other countries [29-31].

6 Conclusion

Nitrosamines produced as byproducts of WTP operations is a global water quality concern. The use of chloramines as a disinfectant provides a significant pathway for the formation of nitrosamines. Reduction of nitrosamine formation potential begins with proper assessment of source waters that are being treated for drinking purposes. Identifying point sources of pollution and determining land use within a source water catchment provides information on the type and amount of precursors that could be present in a receiving source water. To further reduce nitrosamine formation potential during water treatment, chloramination WTP operators need to follow procedures that remove precursors before chloramine disinfection. By adopting this practice, and implementing source water protection strategies, there will be less risk of

consuming nitrosamine contaminated drinking water in areas supplied by chloraminated distribution systems.

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References

1. I.M. Schreiber, W.A. Mitch, Environ. Sci. Technol., **40**, 6007-6014, (2006)
2. S.W. Krasner, W.A. Mitch, D.L. McCurry, D. Hanigan, P. Westerhoff, Water Res., **47**, 4433-4450, (2013)
3. W.A. Mitch, D.L. Sedlak, Environ. Sci. Technol., **36**, 588-595, (2002)
4. A.D. Shah, W.A. Mitch, Environ. Sci. Technol., **46**, 119-131, (2012)
5. J. Choi, R.L. Valentine, Water Res., **36**, 817-824, (2002)
6. W.A. Mitch, A.C. Gerecke, D.L. Sedlak, Water Res., **37**, 3733-3741, (2003)
7. W.A. Mitch, J.O. Sharp, R.R. Trussell, R.L. Valentine, L. Alvarez-Cohen, D.L. Sedlak, Environ. Eng. Sci, **20**, 389-404, (2003)
8. D. Baytak, A. Sofuoglu, F. Inal, S.C. Sofuoglu, Sci. Total Environ., **407**, 286-296, (2008)
9. W.A. Mitch, D.L. Sedlak, Environ. Sci. Technol., **38**, 1445-1454, (2004)
10. A.C. Gerecke, D.L. Sedlak, Environ. Sci. Technol., **37**, 1331-1336, (2003)
11. W. Chen, T.M. Young, Environ. Sci. Technol., **42**, 1072-1077, (2008)
12. S.W. Krasner, P. Westerhoff, B. Chen, B.E. Rittmann, S. Nam, G. Amy, Environ. Sci. Technol., **43**, 2911-2918, (2009)
13. C.G. Russell, R.A. Brown, K. Porter, D. Reckhow, J. AWWA., **109**, 226-242, (2017)
14. S.T.Y. Tong, W. Chen, J. Environ. Manage., **66**, 377-393, (2002)

15. D. Khiari, J. AWWA, **109**, 38-42, (2017)
16. ATSDR, Toxicological profile for n-nitrosodimethylamine, (U.S. Public Health Service, U.S. Environmental Protection Agency, 1989)
17. R. Klein, Toxicology, **23**, 135-147, (1982)
18. S.S. Mirvish, P. Issenberg, H.C. Sornson, **56**, 1125-1129, (1976)
19. F. Sacher, C. Schmidt, C. Lee, U. von Gunten, Strategies for minimizing nitrosamine formation during disinfection, (Denver, CO, 2008)
20. D. Hanigan, J. Zhang, P. Herckes, S.W. Krasner, C. Chen, P. Westerhoff, Environ. Sci. Technol., **46**, 12630-12639, (2012)
21. W.A. Mitch, S.W. Krasner, P. Westerhoff, A. Dotson, Occurrence and formation of nitrogenous disinfection by-products, (Water Research Foundation, Denver, CO, 2009)
22. J.M. Boyd, S.E. Hrudey, S.S. Richardson, X.-F. Li, Trends Analyt. Chem., **30**, 1410-1421, (2011)
23. C.G. Russell, N.K. Blute, S. Via, X. Wu, Z. Chowdhury, J. Am. Water Works Assoc., **104**, 57-58, (2012)
24. S.W. Krasner, P. Westerhoff, W.A. Mitch, J. Skadsen, Case studies on nitrosamine formation and control at full-scale drinking water treatment plants, (AWWA Water Quality Technology Conference, Denver, CO, 2012)

25. G. Dillon, S. Blake, P. Rumsby, L. Rockett, T. Hall, P. Jackson, A. Rawlinson, NDMA: concentrations in drinking water and factors affecting its formation, (Defra Report 7348, London, 2008)
26. M.R. Templeton, Z. Chen, J. Water Supply: Res. Technol. Aqua, **59**, 277-283, (2010)
27. G. Newcombe, J. Morran, J. Culbert, N. Slyman, J. Leach, C. Kapralos, Occurrence and management of NDMA and other nitrogenous disinfection by-products in Australian drinking and recycled waters, (WQRA Project 1018 Milestone 5, Adelaide, South Australia, 2012)
28. D. Liew, K.L. Linge, C. Joll, A. Heitz, R. Trolie, L. Breckler, R. Henderson, J.W.A. Charrois, Formation of nitrogenous disinfection by-products (N-DBPs) in raw and treated drinking water, (OZ Water Conference, 2011)
29. C. Wang, C. Chen, J. Wang, X. Zhang, Occurrence of n-nitrosamines in drinking water treatment plants (DWTPs) in China, (School of Environment, Tsinghua University, Beijing, China, 2011)
30. C. Wang, C. Chen, X. Zhang, J. Wang, Characterization of natural organic matter as precursors for nitrosamines: hydrophobicity, molecular weight and fluorescence, (International Water Association Specialty Conference on Natural Organic Matter, 2011)

31. E. Bei, Y. Shu, S. Li, X. Liao, J. Wang, X. Zhang, C. Chen, S. Krasner, *Water Res.*, **98**, 168-175, (2016)

CHAPTER 2

Chapter 2 has been formatted for submission to Chemosphere.

N-nitrosamine analysis using standard extraction techniques and common analytical instrumentation

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Highlights

- A GC-MS method was established to detect 9 N-nitrosamines from water extracts.
- LOD was found to be between 1-2 µg/L.
- Further development of method required to improve chromatogram precision.

Abstract: N-nitrosamines are a group of contaminants of emerging concern that have been classified as probable human carcinogens in multiple risk assessments. N-nitrosamines are frequently found as by-products from water treatment practices, posing a large risk to consumers. Many studies have found important formation pathways for several N-nitrosamines, however more information is required to fully understand those processes. Typical N-nitrosamine analyses involve costly methods, leaving many facilities or institutions resorting to other approaches for analysis. The purpose of this study was to design a lower-cost, and widely available method to be used for high-level N-nitrosamine analysis. Although this method was capable of detecting all nine targeted N-nitrosamines, further development is required to establish method detection limits (MDL) and analyte calibrations. Analytical precision improvements, and potential method applications were also considered.

Keywords: N-nitrosamines, by-products, water, water quality, analysis, method, formation potential

1. Introduction

N-nitrosamines are a group of potent carcinogens (U.S. EPA, 1986; IARC, 1987) that have been widely studied since their earliest detection in drinking water in the 1970's (Wolff & Wasserman, 1972). Presence of N-nitrosamines in drinking water is of significant concern because of their carcinogenic, mutagenic, and teratogenic properties (Lin, 1990; Loeppky, 1994). Many studies have been conducted to identify formation mechanisms of certain N-nitrosamine species during water treatment (Choi & Valentine, 2002; Mitch & Sedlak, 2002; Mitch & Sedlak, 2004; Schreiber & Mitch, 2006; Fan et al., 2018). Although major formation pathways have been identified, there is still a need to conduct formation potential studies as new findings emerge (Farré et al., 2019). Typically, N-nitrosamine studies follow U.S. EPA Method 521 for analysis because of its high degree of precision and low-level detection limits (Munch & Bassett, 2004; Charrois et al., 2007; Russel et al., 2012; Bei et al., 2016). However, very few facilities have affordable access to the analytical equipment required by U.S. EPA Method 521, leaving those facilities to look elsewhere to complete their analysis.

The purpose of this study was to develop a cost-effective, and widely available analytical method that can be used for detection of N-nitrosamines at levels greater than 1 µg/L. Liquid-liquid extraction approaches from Method 6410: Extractable Base/Neutrals and Acids from the Standard Methods for the

Examination of Water and Wastewater (SMWW), were combined with gas chromatography mass spectrometry (GC-MS) analysis. Results from this study will show the effectiveness of the proposed method, as well as highlight where alterations can be made. After future establishment of method detection limits (MDL) and target analyte calibrations, this method will be acceptable to use in studies focused on high level formation of N-nitrosamines in drinking water.

2. Materials and methods

2.1. Chemicals and reagents

Analytical-grade N-nitrosamine mix at a concentration of 2000 µg/mL in methanol was purchased from Sigma Aldrich and was used as the analytical standard for development of this method. An N-nitrosamine stock solution was prepared at 20 µg/mL in analytical grade methylene chloride Optima[®] (DCM) purchased from Fisher Scientific. Serial dilutions of the stock solution were made to achieve target N-nitrosamine concentrations during analysis. 10 N laboratory grade sodium hydroxide (NaOH) and sodium sulfate (Na₂SO₄) anhydrous were also purchased from Fisher Scientific.

2.2. Sample preparation

1 L amber bottles were rinsed with DCM, then detergent washed, followed by rinsing with deionized water. Bottles were drained, then baked in a muffle furnace at 270°C for three hours. After bottles were baked and cooled, the

bottles and PTFE caps were rinsed with DCM and allowed to dry before use.

Milli-Q ultrapure deionized water was used as the sample matrix in this detection limit study to avoid signal interferences during analysis. Without prior rinsing with sample matrix, each 1 L sample bottle was filled to no head space then capped. Since the samples did not require to be stored for later processing, all filled sample bottles were immediately extracted.

2.3. Sample extraction

Individual samples were immediately transferred to a 2 L separatory funnel and injected with the target concentration of N-nitrosamine stock solution, then mixed. pH was checked with an Oakton pH spear and adjusted to >11 using laboratory grade NaOH. Sample bottles were filled with 60 mL of DCM, shaken for 30 seconds, then DCM was transferred to the separatory funnel containing the sample. After transfer was complete, the sample was extracted by shaking the separatory funnel for 2 min. A minimum of 10 min was designated to allow solvent and water separation. The solvent extraction steps were performed in triplicate per each sample.

The solvent used to extract each sample was dispensed from the separatory funnel and collected in a clean 250 mL Erlenmeyer flask. The extract was then poured through a chromatographic drying column (400 mm x 19 mm ID) filled with at least 10 cm of Na₂SO₄ and collected in a Kuderna-Danish (KD)

concentration apparatus, constructed from a 500 mL evaporative flask and 10 mL concentrator tube. An additional 20 mL of DCM was used to complete the transfer of sample extract from the chromatographic drying column into the KD apparatus. Upon complete transfer, a three-ball Snyder column was attached to the top of the evaporative flask, and pre-wet with 1 mL DCM. The KD apparatus was placed on a warm water bath (65°C) in a hood and adjusted so the concentrator tube was partially immersed in warm water and the entire bottom surface of the flask was continually bathed in vapor. The extract was concentrated to an apparent 1 mL then removed from the water bath and allowed to cool for a minimum of 10 min. Snyder column was removed and the evaporative flask was rinsed with 1 mL DCM. Evaporative flask was removed from concentrator tube and replaced by a two-ball micro Snyder column. Extract was concentrated to an approximate 0.5 mL then removed from the water bath. Final volume of concentrated extract was immediately adjusted to 1 mL using DCM. Extract was transferred to a PTFE-lined screw cap vial using a clean borosilicate glass syringe then stored at 4°C until analyzed.

2.4. Analytical techniques

N-nitrosamines from sample extracts were chromatographically separated and analyzed using a Shimadzu GC-MS - QP2010SE equipped with an AOC - 20S auto sampler. The analytical column used for this experiment was a Restek®

RTX-VMS (30 m x 0.25 mm x 1.4 μ m). A 1.0 μ L sample was injected into the GC inlet in splitless mode. Injection temperature was set at 260 °C. The GC oven temperature was programmed as follows: initially set to 50 °C and held for 4 min, the oven was ramped at 8 °C/min to a final temperature of 240 °C and held for 5.25 min. The helium gas carrier flow rate was set at 1.0 mL/min. MS interface and ion source temperatures were both set at 260 °C. MS was operated in EI mode with detector voltage set as relative to tuning result. N-nitrosamines were identified in the chromatogram based on their specific retention times (Table 1).

Table 1. Target N-nitrosamines and their associated abbreviations and retention times.

N-nitrosamine	Abbreviation	Retention Time (min)
N-nitrosodimethylamine	NDMA	11.54
N-nitrosomethylethylamine	NMEA	13.66
N-nitrosodiethylamine	NDEA	15.24
N-nitroso-di- <i>n</i> -propylamine	NDPA	18.88
N-nitrosomorpholine	NMOR	19.04
N-nitrosopyrrolidine	NPYR	19.57
N-nitrosopiperidine	NPIP	20.44
N-nitrosodibutylamine	NDBA	22.44
N-nitrosodiphenylamine	NDPhA	27.45

3. Results and discussion

3.1. Chromatogram of the N-nitrosamines

The GC-MS chromatogram for the nine N-nitrosamines (2 μ g/L) is shown in Fig. 1. All nine N-nitrosamines were completely separated, respectively. Other prominent peaks are shown in Fig. 1 and were identified as hydrocarbons.

Further evaluation is required to determine possible sources of the additional peaks.

Results show that the lower molecular weight compounds tend to have shorter retention times, with NDMA exhibiting the shortest and NDPhA the longest (Table 1). It is apparent that some of the N-nitrosamines, e.g., NDMA, NMEA, and NMOR, produced weak signals, therefore it can be declared that limit of detection (LOD) was reached for those target analytes (Thomsen et al., 2003). All other targeted N-nitrosamines produced improved signals, implying that future samples may be prepared with lower standard concentration, e.g., 1 $\mu\text{g/L}$.

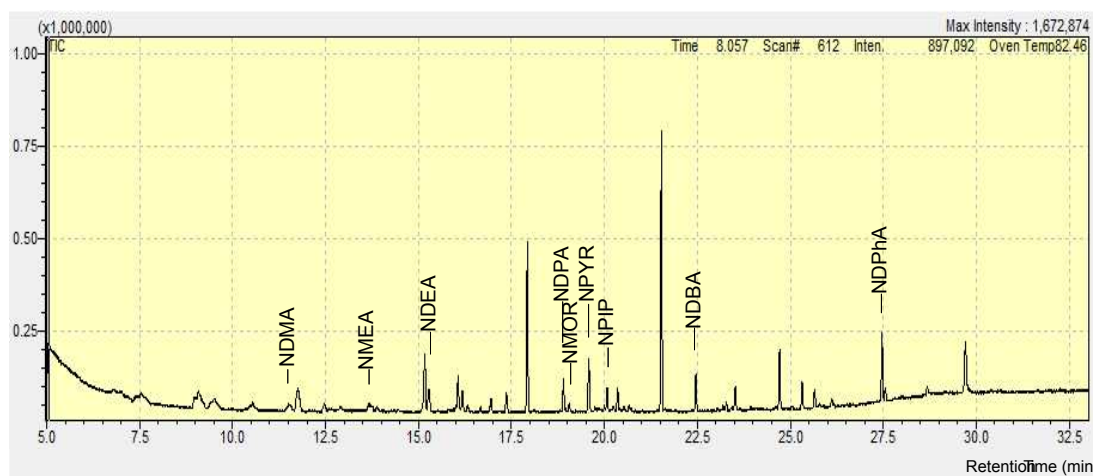


Fig. 1. GC-MS chromatogram of nine N-nitrosamines (2 $\mu\text{g/L}$).

3.2. Method evaluation

As previously mentioned, several of the target analytes produced weak signals at 2 µg/L, signifying LOD. Another important finding was the occurrence of coelution with other prominent peaks, and poor separation, e.g., NDEA, and NPYR. In Fig. 2, we saw poor separation of NDEA and a hydrocarbon, where in Fig. 3, we saw complete coelution of NPYR and a hydrocarbon. It should be noted that without presence of hydrocarbons, coelution and poor separation would not be occurring with NDEA and NPYR peaks. Typically, improved peak separation and signal quality is seen when using enhanced analytical equipment (Fialkov et al., 2007; Kodamatani et al., 2009; Alder et al., 2011; Portolés et al., 2012; Fujioka et al., 2016; Chen et al., 2017), however, to maintain the scope and application of this method, improved sample preparation is required.



Fig. 2. Magnified chromatogram showing poor separation between NDEA and an identified hydrocarbon.

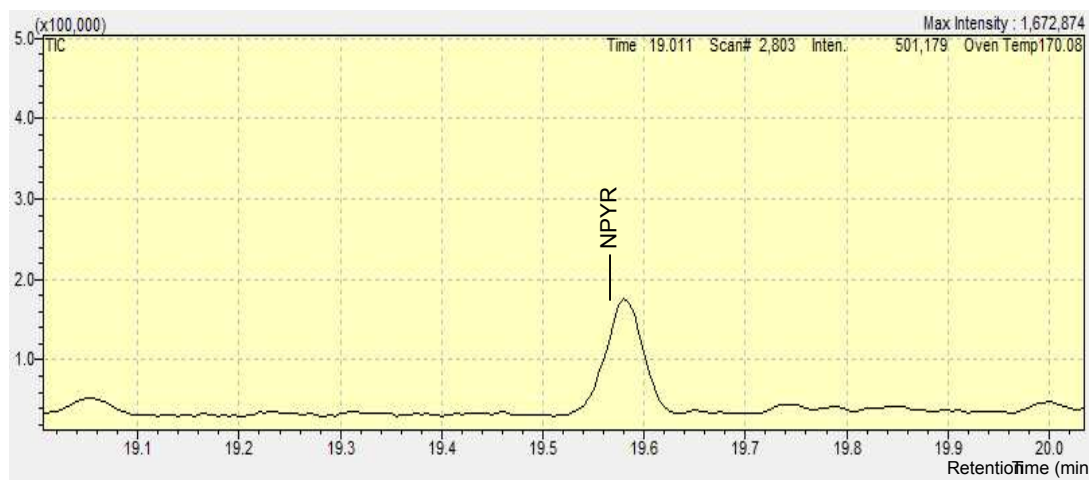


Fig. 3. Magnified chromatogram showing complete coelution between NPYR and an identified hydrocarbon.

Although some implications were present with peak separation, the proposed method was still capable of identifying other N-nitrosamines without any interferences. In fact, Fig. 1 demonstrates the potential for identification and quantification of all target analytes listed in Table 1. To avoid future interferences from unwanted chromatographic artifacts, it is recommended that all non-volumetric experimental glassware be baked at a higher temperature (400 °C) for 1 hr. Should interferences still persist, an evaluation must be made on the quality of the experimental sample matrix.

3.3. Method application

Application of this method to quantify unknown levels of N-nitrosamines is possible. Further calibrations, and extractions are required to establish method detection limits (MDL) for each target analyte. After a preliminary assessment, 1 -

2 µg/L appears to be the LOD for several of the N-nitrosamines. Because of this limitation, this method will not prove useful for quantifying N-nitrosamines in the low ng/L range, which is an important requirement when performing N-nitrosamine studies (Kodamatani et al., 2009; West et al., 2016; Fujioka et al., 2016; Chen et al., 2017; Fan et al., 2018). However, this method could be valuable in particular cases such as formation potential studies, where high N-nitrosamine concentrations (>1 µg/L) are expected (Mitch & Sedlak, 2002; Choi & Valentine, 2002; Choi & Valentine 2003; Mitch et al., 2003; Mitch et al., 2005; Chen & Young; 2008; West et al., 2016).

4. Conclusions

This analytical method was designed to serve as a cost-effective and widely available tool for performing N-nitrosamine studies. We found that this method was capable of analyzing all N-nitrosamines listed in Table 1. In a sample spiked with 2 µg/L N-nitrosamines, certain target analytes such as NDMA, NMEA, and NMOR produced weak signals, suggesting possible LOD. Other N-nitrosamines, e.g., NDEA, NDPA, NPIP, NDBA, and NDPhA, produced improved signals at 2 µg/L, creating a need for further LOD studies. It is critical that coelution be noted, explaining the interferences between unwanted artifacts and N-nitrosamine signals, particularly in the case of NPYR. To resolve the issue of unwanted compounds in the finished sample, thorough cleaning and baking of

experimental glassware is suggested. If unwanted compounds still persist, the sample matrix quality must be evaluated.

Application of this method in other research is feasible, particularly in formation potential studies where it is presumed high levels of N-nitrosamines will form from known reactants. In regards capturing ng/L levels of N-nitrosamines, this method will not perform effectively. Therefore, any studies targeting the occurrence of N-nitrosamines in natural water, treated water, or wastewater, should resort to lower detection limit analytical methods.

Acknowledgements

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References

- Alder, L., Greulich, K., Kempe, G., Vieth, B., 2011. Residue analysis of 500 high priority pesticides: better by GC-MS or LC-MS/MS. *Mass. Spec. Rev.* 25, 838-865.
- Bei, E., Liao, X., Meng, X., Li, S., Wang, J., Sheng, D., Chao, M., Chen, Z., Zhang, X., Chen, C., 2016. Identification of nitrosamine precursors from urban drainage during storm events: a case study in southern China. *Chemos.* 160, 323-331.
- Charrois, J.W.A., Boyd, J.M., Froese, K.L., Hrudey, S.E., 2007. Occurrence of N nitrosamines in Alberta public drinking-water distribution systems. *J. Environ. Eng. Sci.* 6, 103-114.
- Chen, W., Young, T.M., 2008. NDMA formation during chlorination and chloramination of aqueous diuron solutions. *Environ. Sci. Technol.* 42, 1072-1077.
- Chen, W., Li, X., Huang, H., Zhu, X., Jiang, X., Zhang, Y., Cen, K., Zhao, L., Liu, X., Qi, S., 2017. Comparison of gas chromatography-mass spectrometry and gas chromatography tandem mass spectrometry with electron ionization for determination of N-nitrosamines in environmental water. *Chemos.* 168, 1400-1410.

- Choi, J., Valentine, R.L., 2002. Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloramine: a new disinfection by-product. *Wat. Res.* 36, 817-824.
- Choi, J., Valentine, R.L., 2003. N-nitrosodimethylamine formation by free chlorine-enhanced nitrosation of dimethylamine. *Environ. Sci. Technol.* 37, 4871-4876.
- Fan, C., Lin, T., 2018. N-nitrosamines in drinking water and beer: detection and risk assessment. *Chemos.* 200, 48-56.
- Farré, M.J., Jaén-Gil, A., Hawkes, J., Petrovic, M., Catalán, N., 2019. Orbitrap molecular fingerprint of dissolved organic matter in natural waters and its relationship with NDMA formation potential. *Sci. Tot. Environ.* 670, 1019-1027.
- Fialkov, A.B., Steiner, U., Lehotay, S., Amirav, A., 2007. Sensitivity and noise in GC-MS: achieving low limits of detection for difficult analytes. *Int. J. Mass. Spec.* 260, 31-48.
- Fujioka, T., Takeuchi, H., Tanaka, H., Nghiem, L.D., Ishida, K.P., Kodamatani, H., 2016. A rapid and reliable technique for N-nitrosodimethylamine analysis in reclaimed water by HPLC photochemical reaction-chemiluminescence. *Chemos.* 161, 104-111.

International Agency for Research on Cancer (IARC), 1987. Evaluation of the
Carcinogenic Risks to Humans.

Kodamatani, H., Yamazaki, S., Saito, K., Amponsaa-Karikari, A., Kishikawa, N.,
Kuroda, N., Tomiyasu, T., Komatsu, Y., 2009. Highly sensitive method for
determination of N nitrosamines using high-performance liquid
chromatography with online UV irradiation and luminol
chemiluminescence detection. J. Chrom. A. 1216, 92-98.

Lin, J.K., 1990. Nitrosamines as potential environmental carcinogens in man. Clin.
Biochem. 23, 67-71.

Loeppky, R.N., 1994. Nitrosamine and N-nitroso compound chemistry and
biochemistry. Am. Chem. Soc. 1-18.

Mitch, W.A., Sedlak, D.L., 2002. Formation of N-nitrosodimethylamine (NDMA)
from dimethylamine during chlorination. Environ. Sci. Technol. 36, 588
595.

Mitch, W.A., Gerecke, A.C., Sedlak, D.L., 2003. A N-Nitrosodimethylamine
(NDMA) precursor analysis for chlorination of water and wastewater. Wat.
Res. 37, 3733-3741.

Mitch, W.A., Sedlak, D.L., 2004. Characterization and fate of N
nitrosodimethylamine precursors in municipal wastewater treatment
plants. Environ. Sci. Technol. 38, 1445-1454.

- Mitch, W.A., Oelker, G.L., Hawley, E.L., Deeb, R.A., Sedlak, D.L., Minimization of NDMA formation during chlorine disinfection of municipal wastewater by application of pre formed chloramines. *Environ. Eng. Sci.* 22, 882-890.
- Munch, J.W., Bassett, M.V., 2004. In: Agency (Ed.), Determination of Nitrosamines in Drinking Water by Solid Phase Extraction and Capillary Column Gas Chromatography with Large Volume Injection and Chemical Ionization Tandem Mass Spectrometry (MS/MS). EPA, US.
- Portolés, T., Cherta, L., Beltran, J., Hernández, F., 2012. Improved gas chromatography tandem mass spectrometry determination of pesticide residues making use of atmospheric pressure chemical ionization. *J. Chrom. A* 1260, 183-192.
- Russel, C.G., Blute, N.K., Via, S., Wu, X., Chowdhury, Z., 2012. Nationwide assessment of nitrosamine occurrence and trends. *J. AWWA* 104, 205-217.
- Schreiber, I.M., Mitch, W.A., 2006. Nitrosamine formation pathway revisited: the importance of chloramine speciation and dissolved oxygen. *Environ. Sci. Technol.* 40, 6007-6014.
- Standard Methods for the Examination of Water and Wastewater (SMWW), Extractable Base/Neutrals and Acids.
- Thomsen, V., Schatzlein, D., Mercurio, D., 2003. Limits of detection in spectroscopy. *Spectro.* 18, 112-114.

United States Environmental Protection Agency (U.S. EPA), 1986. Guidelines for
Carcinogen Risk Assessment.

West, D.M., Wu, Q., Donovan, A., Shi, H., Ma, Y., Jiang, H., Wang, J., 2016. N
nitrosamine formation by monochloramine, free chlorine, and peracetic
acid disinfection with presence of amine precursors in drinking water
system. Chemos. 153, 521-527.

Wolff, W.A., Wasserman, A.E., 1972. Nitrates, nitrites, and nitrosamines. Sci. 177,
15-19.

CHAPTER 3

Chapter 3 has been formatted for submission to Water.

N-nitrosodimethylamine (NDMA) Formation From Treatment of Seasonally and Spatially Varying Source Water

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Abstract: N-nitrosodimethylamine (NDMA) is a disinfection by-product (DBP) that has been classified as a probable human carcinogen in multiple risk assessments. The presence of NDMA in drinking water is widespread and dependent on factors such as source water, disinfectant type, precursors, and water treatment strategies. Many NDMA formation studies exist, however, few discuss the impact of seasonal and spatial variability in natural source water and its potential to form NDMA during water treatment. The objectives of this study are to investigate NDMA formation potential in a modeled monochloramine water treatment plant (WTP) fed by seasonally and spatially varying source water; and to optimize DBP precursor removal by combining conventional coagulation, flocculation, sedimentation, and filtration with additional granular activated carbon filtration techniques. Using novel approaches to NDMA analysis, it was found that NDMA formation was significantly dependent on source water type and monochloramine contact time (CT); e.g., at 24 hr CT, Cork Brook produced 12.2 ng/L NDMA and Bailey Brook produced 4.2 ng/L NDMA, compared with 72 hr CT, Cork Brook produced 4.1 ng/L NDMA and Bailey Brook produced 3.4 ng/L NDMA. No direct correlations were found between traditional DBP precursors such as total organic carbon and total nitrogen, and the formation of NDMA. The bench-top treatment system proved to be highly effective at removing

traditional DBP precursors, highlighting the need for WTPs to alter their current treatment methods to best accommodate the complex system of DBP control.

Keywords: NDMA; by-product formation; source water; natural water; precursors; treatment; water quality

1. Introduction

N-nitrosamines are a group of contaminants of emerging concern that may be present in drinking water as by-products from water treatment plant (WTP) operations [1-6]. Significant influences on the formation of N-nitrosamines in drinking water include source water impairment before treatment, e.g., industrial, wastewater, and septic system effluents [6,7]. Presence of N-nitrosamines in drinking water is of particular concern because of their carcinogenic, mutagenic, and teratogenic properties [8,9]. N-nitrosodimethylamine (NDMA, $C_2H_6N_2O$), and several other N-nitrosamines are classified as probable carcinogens based on domestic and international assessments [10,11]. To date, no federal regulatory limits have been established for NDMA and other N-nitrosamines in drinking water, although some states have created their own guidelines, e.g., California and Massachusetts, in 2002 and 2004 respectively [12,13]. Many studies were developed to understand the mechanics of NDMA formation during water treatment [1,2,4,14-16]. However, little research has evaluated NDMA formation

from the treatment of seasonally and spatially varying source water during normal environmental conditions.

Primary NDMA formation pathways involve reactions between NDMA precursors found in source water, with the disinfectant used during treatment [1-4,17,18]. The degree to which NDMA forms under these conditions is significantly dependent on influent source water, type of disinfectant, pH, and temperature [2,6,18-20]. More specifically, monochloramine, one of the widely used disinfectants, is documented to be one of the most critical reactants that lead to NDMA formation [1,4,21,22]. Potential NDMA precursors such as dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and natural organic matter (NOM) are also significantly influenced by land use and seasonal variations [23-26].

Traditionally, formation of disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) can be controlled by precursor removal before disinfection [27-29]. Conventional WTP processes used for removing precursors include coagulation and flocculation, sedimentation, and filtration [30]. Other studies have been conducted to address the impact of using additional filtration techniques for controlling DBP precursors [31,32]. Little information is known about the impact of water treatment processes on

potential NDMA precursor removal, and the relationship it has with NDMA formation following monochloramine disinfection.

To address this issue, we investigated the formation potential of NDMA in a modelled chloramination WTP fed by seasonally and spatially varying source water. To enhance the reduction of potential NDMA precursors, conventional water treatment methods were combined with additional filtration techniques. This work will also address the impact of regional WTP operations and their potential to form NDMA under specific treatment scenarios. Results from this study will serve as the foundation for further NDMA research as it relates to drinking water treatment of regionally sourced waters.

2. Materials and Methods

2.1 Field Site Locations

The field sites identified in Figure 1 were chosen for this study to demonstrate impact of spatial variability on source water quality. Both locations are headwater streams for major reservoirs in Newport and Scituate, Rhode Island. Source water entering Newport WTPs, e.g., Bailey Brook, has received higher loads of nutrients from a variety of sources due to its location in an urban area [33]. Cork Brook, although forested [34], has experienced seasonally high loadings of precursors, particularly during intense precipitation events. It is expected that the different land use activities associated with each field site will

produce varying levels of precursors [19,24,26], later affecting the formation of NDMA upon water treatment.

2.2 Sample Collection

Samples were collected during Summer 2018 (June-August), Fall 2018 (September-November), and Spring 2019 (March-May) after precipitation events greater than 0.5 inches [35]. During each sampling event at both field sites, one sample was collected in a clean five gallon plastic jerry can. After collection, samples were returned to The University of Rhode Island Hydrology and Environmental Water Quality Research Laboratory for freezer storage (below 0 °C) until sample processing.



Figure 1. Map of the state of Rhode Island, USA. Field sample locations identified by red circles on map. Rhode Island map to scale.

2.3 Sample Processing

Each field sample was processed two times using a benchtop water treatment system (Figure 2) to simulate water treatment and distribution at a municipal or metropolitan scale. Flocculation, coagulation, and sedimentation phases of water treatment were achieved using a Lovibond ET 750 Floc Tester, equipped with 2 L Phipps & Bird square B-Ker². Beakers were filled to 2 L mark

with thawed sample, then dosed with 25 mg/L of ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) (ferrous iron 0.0%–0.3%, ferric iron 12.5%–13.5%). pH was adjusted to 5.6 using 1 N laboratory grade sulfuric acid. Floc Tester blade height was adjusted to 2.25 inches from the bottom of the beaker, then mixed at 250 rpm for 10 min. After allowing floc to settle for 30 min, the sample was mixed at 30 rpm for 30 min, then settled for ≥ 1 hr. Using a Fisher Scientific Variable Flow peristaltic pump, water above the settled particulate layer was pumped through acrylic tubing filled with beds of 0.45–0.55 mm homogenized silica sand, and 0.95–1.05 mm cleaned anthracite, under-bedded by 1/4" washed gravel. A Cole-Parmer Gear Pump Drive peristaltic pump was used to pump effluent from the dual-media column filter into a borosilicate glass column filled with 20–40 mesh granular activated carbon (GAC). Addition of the GAC column filter to the treatment system was to enhance precursor removal before disinfection. Both columns were selected to have an empty bed contact time (EBCT) of 10 min [31]. During each run of processing, two samples were collected in 500 mL amber glass jars with no headspace from raw water influent and post-filtration effluents, and one sample was collected in a 300 mL amber glass jar from the same influent and effluents. All processed samples were kept in refrigerator storage (4 °C) until disinfection.

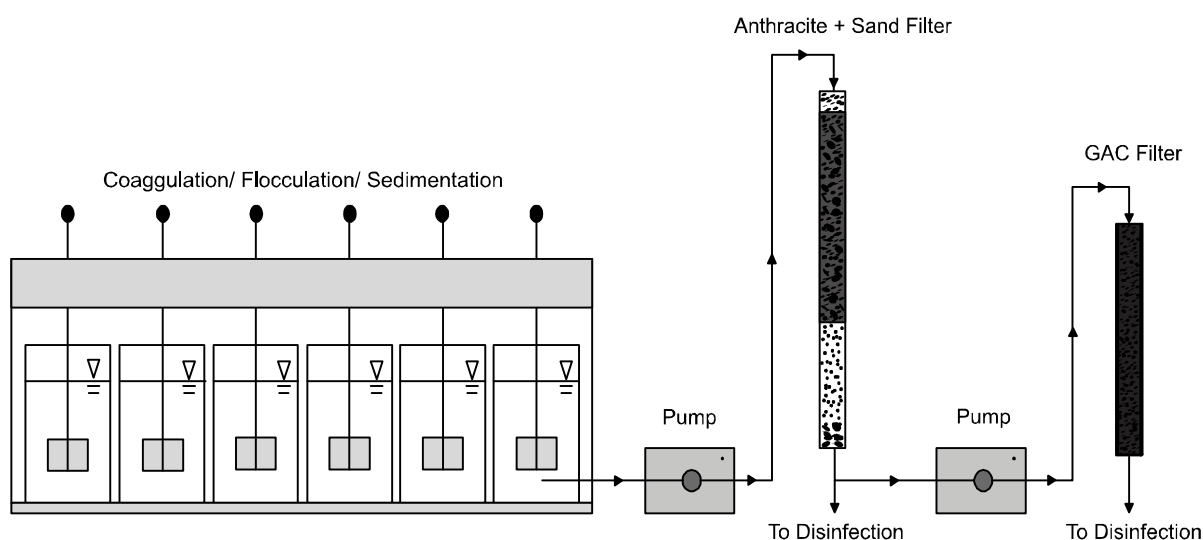


Figure 2. Flow-scheme of benchtop water treatment system.

2.4 Monochloramine Disinfection

All 500 mL processed samples were removed from refrigeration and brought to room temperature (25 °C), and then pH was adjusted to between 9 and 10 using 1 N laboratory grade sodium hydroxide (NaOH). Pre-formed monochloramine (NH_2Cl) stock solution was prepared from diluted solutions of sodium hypochlorite (NaOCl) and ammonium chloride (NH_4Cl). The Cl_2/N ratio was 1:1.2, and pH was adjusted to ≥ 8 with 1 N laboratory grade NaOH to prevent the decay of NH_2Cl into dichloramine (NHCl_2) and trichloramine (NCl_3) from excess free chlorine, and low pH values [28,36]. The stock solution was aged in 1 L amber jars with no headspace for 1 hr in darkness at 25 °C, to guarantee complete NH_2Cl formation. Stock solutions were freshly prepared before sample disinfection, and monochloramine dose accuracy was tested using a HACH SL 1000 probe. The NH_2Cl stock solution was injected into each processed sample

to achieve a simulated water treatment dose of 4 mg/L NH_2Cl . Once dosed with NH_2Cl , samples were aged to an allotted contact time (CT) of 24 or 72 hr in the dark, at 25 °C. After disinfection CT was achieved, NH_2Cl residuals were measured using a HACH SL 1000 probe, and then samples were quenched with 100 mg sodium thiosulfate anhydrous.

2.5 NDMA Analysis Preparation

Disinfected samples were filtered using GE Whatman 0.45 μm sterile PTFE filters. About 1 mL of disinfected sample was filtered directly into clear, sterile 2 mL vials. All sample vials were immediately packed into an insulated cooler with freezer packs, then express-shipped to Kagoshima University, Japan for NDMA analysis.

2.6 Analytical Techniques

2.6.1. Precursor analysis

Precursors selected for this experiment were total organic carbon (TOC) and total nitrogen (TN). The precursors were analyzed using a Shimadzu TOC-L/TN-M unit equipped with an OCT-L autosampler. 1 M TOC and TN stock solutions were prepared from potassium nitrate (KNO_3) and potassium hydrogen phthalate ($\text{C}_8\text{H}_5\text{KO}_4$). Calibration standard was prepared by combining 0.1 M KNO_3 , 0.1 M $\text{C}_8\text{H}_5\text{KO}_4$, and 0.05 M hydrochloric acid (HCl). Serial dilutions of calibration standard were prepared to meet the needs of the expected TOC and

TN concentration range. The analytical method performed simultaneous analysis of TOC and TN.

2.6.2. NDMA analysis

Concentrations of NDMA was analyzed and determined using a high-performance liquid chromatography-inline anion exchange reaction-photochemical reaction-chemiluminescence (HPLC-AEM-PR-CL) [37,38]. The description below was adopted from [39] for a concise explanation of the applied analytical technique:

1. separation of NDMA with an octadecylsilyl column as part of high-performance liquid chromatography (HPLC)
2. photolysis of NDMA with UV light irradiation to form peroxynitrite
3. chemiluminescence detection

The analytical system consisted of a Shimadzu DGU-20A₃ degasser, an SIL-20AC autosampler, a CTO-20AC column oven (40 °C), a coupled Capcell Pak C₁₈ MGII column (5 µm, 4.6 mm ID, 250 mm + 100 mm length), a CL-2027 chemiluminescence detector, a Chromato-PRO data processor, and a homemade photochemical reactor comprised of a low-pressure mercury lamp (15 W, CL-15, National, Tokyo, Japan) [39].

2.7 Statistical Methods

All statistical analysis was completed using OriginPro software. Box plots and scatter plots were generated to demonstrate precursor removal and NDMA formation. Main and interaction effects on the concentrations of NDMA, TOC, and TN were assessed using 3-way ANOVA. The three-way analysis of variance model can be written as:

$$Y_{ijkt} = \mu + \alpha_i + \beta_j + \gamma_k + (\alpha\beta)_{ij} + (\alpha\gamma)_{ik} + (\beta\gamma)_{jk} + (\alpha\beta\gamma)_{ijk} + \varepsilon_{ijkt}$$

where the magnitude of any observation Y_{ijkt} can be affected by several possible influences. μ is the overall mean, α_i is the influence of the i^{th} category of the column variable, β_j is the influence of the j^{th} category of the column variable, and γ_k is the influence of the k^{th} category of the column variable. Interaction effects from the combination of column variables are denoted by terms $(\alpha\beta)_{ij}$, $(\alpha\gamma)_{ik}$, and $(\beta\gamma)_{jk}$. The term $(\alpha\beta\gamma)_{ijk}$ is called a three-way interaction term, and ε_{ijkt} is the residual error term.

Significance level $\alpha = 0.05$ was set for all calculations to define the probability of concluding that a difference between groups exists when there is no actual difference. Limitations of ANOVA excluded a fourth main effect from

the analysis. Adjusting for this confine, separate ANOVA tables were generated to represent NDMA formed from treatment of the two source waters.

3. Results and Discussion

3.1 NDMA Formation

This study was designed to model the formation of NDMA from treatment of local source waters using chloramine water treatment techniques. The aim behind the study design was to demonstrate that if local WTPs used chloramine as a primary disinfectant, then the product water sent into distribution would contain low levels of NDMA. Seasonal and spatial variations were considered as possible effects, and precursor removal before disinfection was also considered. Based on previous NDMA formation potential studies, it was expected that after longer monochloramine CT higher concentrations of NDMA would form [18,21,22,40]. In this experiment, we found that only Cork Brook produced higher concentrations of NDMA during the first 24 hr of CT when compared to the 72 hr CT (Figure 3). Scavenging of NDMA precursors by other DBPs is a possibility given that residual chloramine decreased consistently over 72 hr; however, it is speculated that if scavenging were to occur, there would not be a spike of NDMA in the Cork Brook 24 hr CT samples [41].

There was a substantial difference in average NDMA formed between Cork Brook (12.2 ng/L) and Bailey Brook (4.2 ng/L) in the 24 hr CT samples

(Figure 3a): however, the difference between the two averages noticeably decreased in the 72 hr CT samples (Figure 3b). This effect could be explained by NDMA precursors being site-specific and influenced by several factors [42-45]. To determine the processes leading to NDMA reduction over longer CT, further studies are required. It is also noteworthy that the 72 hr CT samples still produced higher average levels of NDMA in Cork Brook (4.1 ng/L) than Bailey Brook (3.4 ng/L), suggesting that the precursors associated with NDMA formation are more frequently associated with forested areas rather than areas of urban influence [46-50].

In previous NDMA formation studies, known precursors were used as reactants with varying doses of monochloramine, resulting in increasing NDMA concentrations with respect to time [18,21,22,40]. The results described in this study are contradictory to traditional NDMA formation potential theory but are best justified by the experimental design. The experimental approach focused on using natural environmental water with potentially very low concentrations of NDMA precursors. Although the results are specific to Rhode Island based source water, they are not representative of all other North East United States source water, therefore, further studies are required to understand NDMA

formation potential at other regional locations.

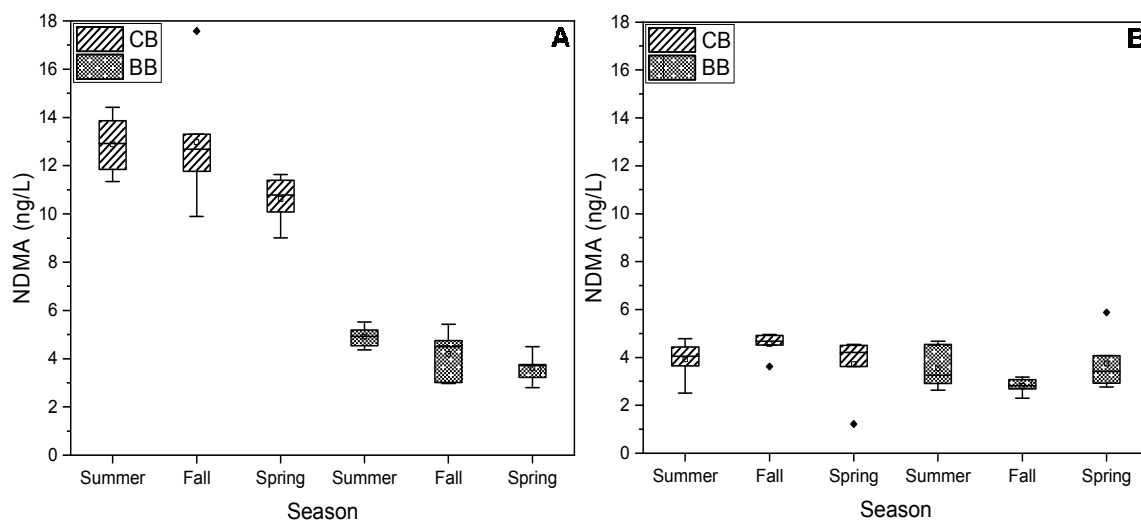


Figure 3. NDMA concentrations in product water after 24 hr (A) and 72 hr (B) monochloramine CT, corresponding to sample site and season. Plots based off of all NDMA concentrations regardless of where the sample was collected from the treatment system. CB = Cork Brook, BB = Bailey Brook.

3.2 Seasonal Precursor Presence

Seasonal influence on concentrations of TOC and TN was substantial (Figure 4). However, TOC and TN concentrations had no apparent effect on the formation of NDMA (Figure 5). This finding supports claims that no significant relationships exist between NDMA and dissolved organic carbon (DOC), natural organic matter (NOM), or TN, and provides further evidence that NDMA has a very complex formation pathway [40,42-44]. The NDMA precursor fingerprinting study by [45] explained that certain aliphatic, as well as peptide and lipid-like compounds are responsible for the majority of NDMA formation in natural

waters, and the origin of those constituents is likely from wastewater effluents.

The likelihood that both Cork Brook and Bailey Brook source water is being impacted by wastewater effluent is low, therefore creating a need for future investigation into precursor identification at the selected field sites.

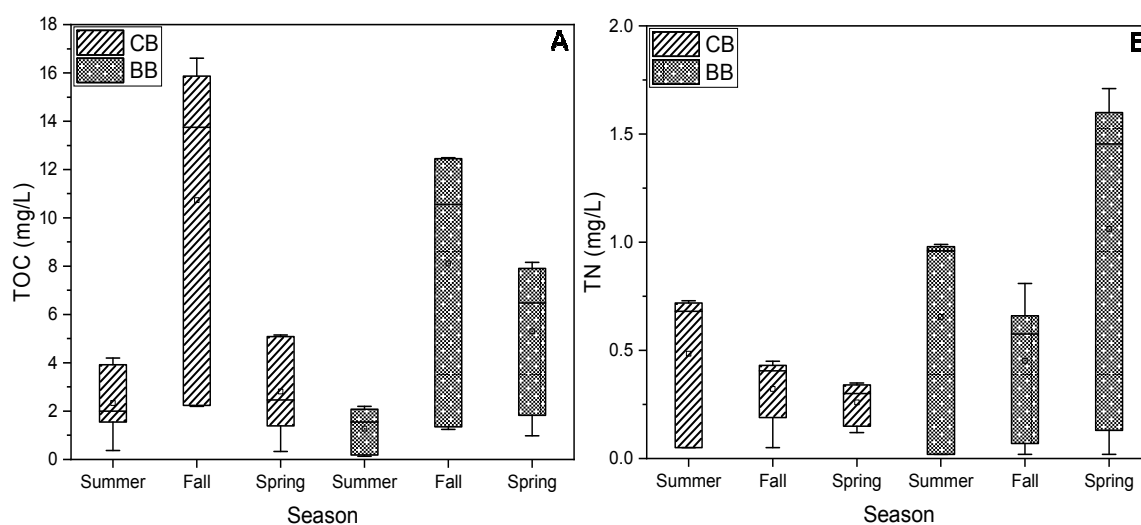


Figure 4. TOC (A) and TN (B) concentrations of processed samples before disinfection, corresponding to sample site and season. Plots based off of all TOC and TN concentrations regardless of where the sample was collected from the treatment system. CB = Cork Brook, BB = Bailey Brook.

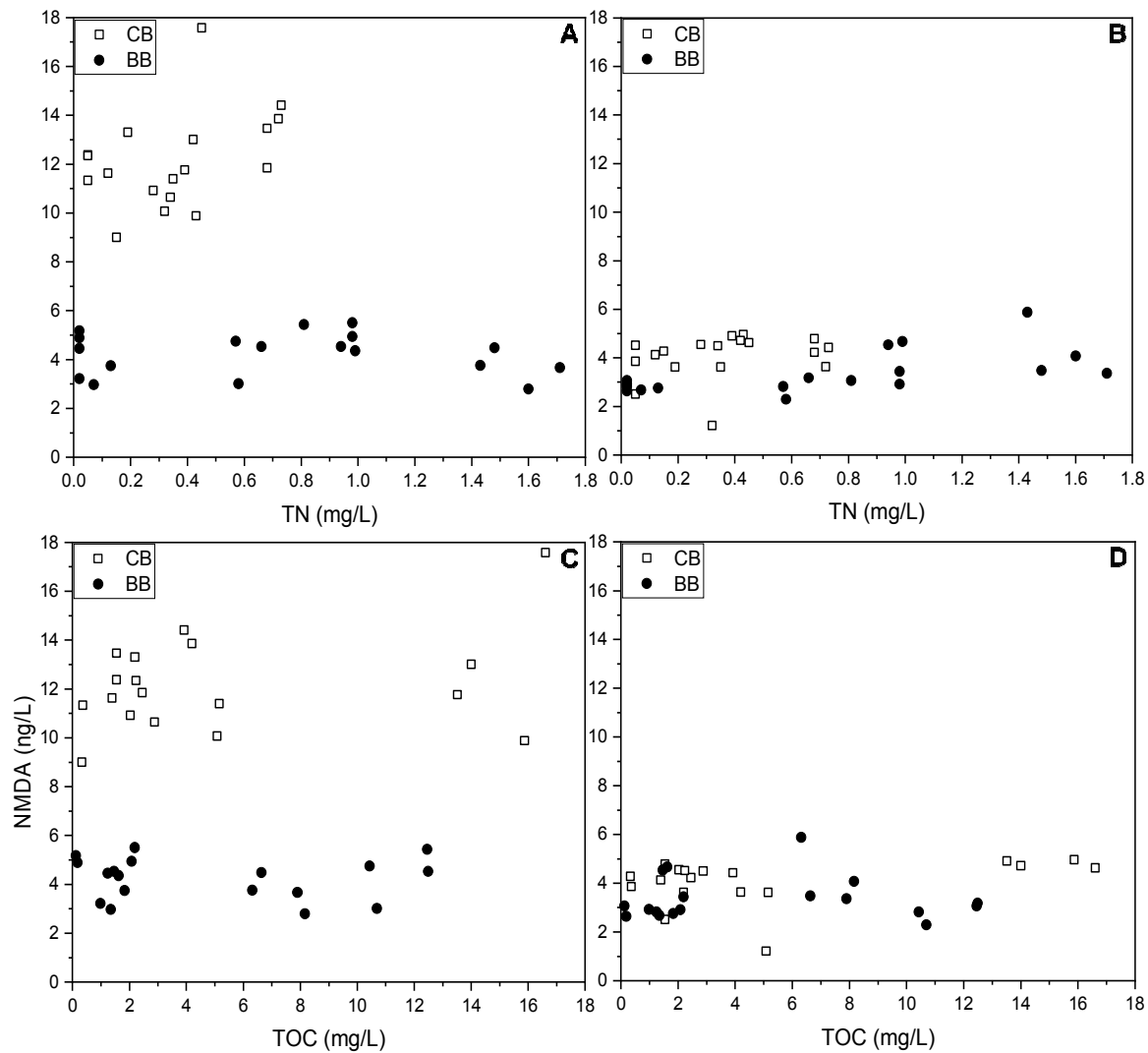


Figure 5. Scatter plots showing no relationships between TN and NDMA, and TOC and NDMA. (A), (C) = 24 hr CT; (B), (D) = 72 hr CT. CB = Cork Brook, BB = Bailey Brook.

3.3 Evaluation of Bench-top Treatment Efficacy

3.3.1. Precursor removal

In order to assess bench-top treatment system efficacy, precursor concentrations were quantified in samples collected from three main points in the system, e.g., raw water influent (R), post-dual-media filtration effluent (F), and post-dual-media filtration + GAC filtration effluent (GAC). At alpha level of 0.05, Figure 6 shows significant differences in precursors concentrations as source water passes through the treatment system. Also noted in Figure 6, there is a negative correlation between the precursors concentration and the place in the treatment system where the sample was collected, demonstrating that the bench-top system was effective at removing traditional DBP precursors [51,52]. The addition of a GAC column filter following dual-media filtration proved to be highly effective at reducing TOC and TN to concentrations below 0.25 mg/L.

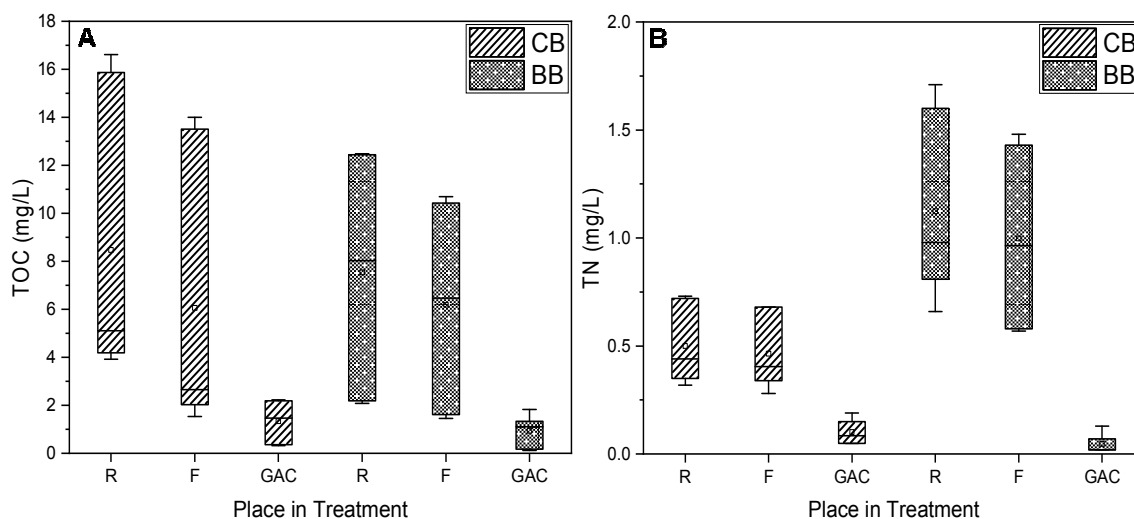


Figure 6. TOC (A) and TN (B) precursor concentrations of processed samples, corresponding to the sample's position in the treatment system. Samples were collected at 3 major phases during treatment: R = untreated raw water; F = dual-media filtration effluent; GAC = dual media filtration + GAC filtration effluent. Plots based off of all TOC and TN concentrations regardless of seasonal sampling event. CB = Cork Brook, BB = Bailey Brook.

3.3.2. NDMA formation potentials

Although there were significant differences in precursor concentrations throughout the treatment system (Figure 6), there was no apparent relationship with the formation of NDMA at each of the main sampling points of the system: R, F, GAC (Figure 7). Therefore, it cannot be stated that the removal of TOC and TN during water treatment will ultimately reduce the likelihood of forming

NDMA during chloramination. Comparisons were made with other studies to identify what particular group of precursors were driving the reactions that generated NDMA (Table 1). The most significant finding was that NDMA formation has a strong positive correlation with aliphatic, as well as peptide and lipid-like compounds [45]. Since the presence of the aforementioned group of precursors is frequently associated with wastewater impacts [45], other routes of exposure were considered.

The findings from [53,54] state that DOM from forested regions has constituents of hydrophobic and hydrophilic fractions, where the hydrophilic fractions could be composed of carbohydrates, small carboxylic acids, free proteins and peptides. Since NDMA formation was highest in source water collected from the forested watershed during all seasons, it suggests that the findings from [45,53,54] have potentially identified the most influential group of NDMA precursors in this experiment. Furthermore, since this particular group of precursors is hydrophilic, there is possible justification as to why the bench-top treatment system was ineffective at NDMA precursor removal, even with the addition of a GAC column.

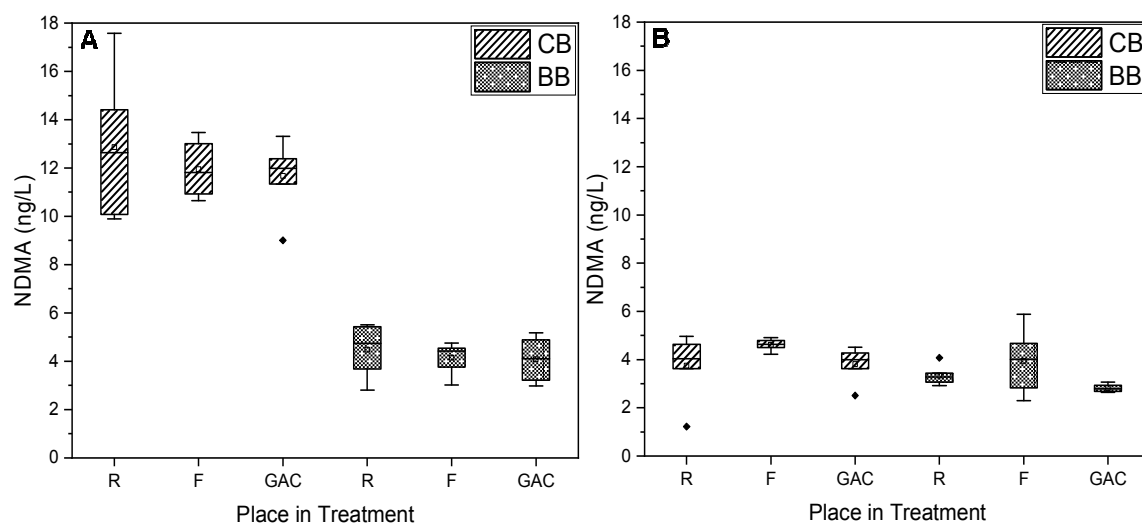


Figure 7. NDMA concentrations in product water after 24 hr (A) and 72 hr (B) monochloramine CT. Samples were collected at 3 major phases during treatment: R = untreated raw water; F = dual-media filtration effluent; GAC = dual media filtration + GAC filtration effluent. Plots based off of all NDMA concentrations regardless of seasonal sampling event. CB = Cork Brook, BB = Bailey Brook.

Table 1. Study comparison on NDMA precursors and their impact on NDMA formation during water treatment.

Study	Source Water	Result	Author
NDMA precursors in natural water	Natural waters from reservoirs, lakes, and groundwaters (U.S.)	NDMA formation has weak correlation to DOC content ($R^2 = 0.41$), however strength of correlation is source dependent. NDMA precursors are a suite of compounds associated with humic substances and other high molecular weight polymers	[40]
NDMA formation in water and wastewater	Untreated natural water (U.S.)	No significant relationship between NDMA formation and natural organic carbon or nitrogen	[42]
Survey of NDMA occurrence in drinking water distribution systems	Lakes, rivers, creeks, and groundwater (Canada)	No apparent trends between NDMA concentrations and DOC, $\text{NH}_3\text{-N}$, NO_3^- , total Kjeldahl nitrogen (TKN), and organic N	[43]
NDMA formation in natural water	Rivers and lakes in (U.S. & Canada)	No significant relationships between NDMA formation and total organic carbon (TOC)	[44]
NDMA formation in natural water, and precursor fingerprinting	Natural reservoirs (Spain)	After fingerprinting dissolved organic matter (DOM), a positive correlation was found between NDMA formation and aliphatic as well as peptide and lipid-like compounds ($r^2 = 0.88$)	[45]

3.3.3. Acceptable NDMA concentrations

NDMA formed as a by-product from the bench-top water treatment system varied significantly with changing CT (Figure 3). There were also significant differences in NDMA produced from each source water site during both CTs (Table 2, 3). Interestingly, source water from Cork Brook produced elevated levels of NDMA (9.1 – 17.6 ng/L) at 24 hour CT during each of the seasonal sampling events (Figure 3a). However, at 72 hr CT, both Cork Brook and Bailey Brook produced NDMA levels that fell within the same range (1.2 – 5.8 ng/L) (Figure 3b). At this time, it is unclear as to why Cork Brook produced a spike in NDMA concentrations at 24 hr CT, then a drop in concentration at 72 hr. No published literature accounts for NDMA formation and degradation during chloramination.

Drinking water leaving a WTP is typically pumped to a storage facility where it resides for days before reaching the consumer [55]. For the case of NDMA formation potential in Rhode Island based source water (Figure 1), these findings are essential. In this experiment, both source waters exposed to 72 hr monochloramine CT resulted in NDMA concentrations below 10 ng/L, complying with regulatory limits already established by California and Massachusetts [12,13]. With the information provided by this study, and future NDMA formation

potential tests of the selected source waters, Rhode Island based WTPs may consider switching to chloramine disinfection to comply with established DBP regulations effectively, and N-DBP regulations to come in the near future.

Table 2. ANOVA table comparing the main and interaction effects of treatment (R, F, GAC), CT, and season on the formation of NDMA in Bailey Brook source water.

Effect	Mean Square *	<i>P Value</i>
Treatment	1.195	0.085
CT	6.769	0.000
Season	1.700	0.035
Treatment * CT	1.003	0.120
Treatment * Season	0.855	0.133
CT * Season	2.260	0.015
Treatment * CT * Season	0.684	0.211

* estimate of population variance based on the variability among a given set of measures

Table 3. ANOVA table comparing the main and interaction effects of treatment (R, F, GAC), CT, and season, on the formation of NDMA in Cork Brook source water.

Effect	Mean Square *	<i>P Value</i>
Treatment	1.218	0.601
CT	590.571	0.000
Season	8.471	0.047
Treatment * CT	2.549	0.356
Treatment * Season	1.638	0.600
CT * Season	3.471	0.252
Treatment * CT * Season	0.271	0.975

* estimate of population variance based on the variability among a given set of measures

4. Conclusions and Future Work

We developed and used a bench-top water treatment system to determine how NDMA formation is influenced by the treatment of seasonally and spatially varying source water. Addressing the influences of precursor interaction with monochloramine disinfectant, we found that the proposed precursors, TOC and TN, had no direct relationship with the formation of NDMA. However, it was noted that the driving precursors are source water dependent and are found particularly in forested watersheds. Also, the precursors that led to the formation of NDMA were not impacted by the bench-top treatment system, suggesting they are likely hydrophilic compounds. CT appeared to be a significant variable when discussing the formation of NDMA, as 72 hr CT led to lower levels of NDMA when compared to 24 hr CT. In fact, the levels of NDMA formed after 72 hr of CT were below regulatory guidelines (10 ng/L) established by California and Massachusetts. This finding suggests that if Rhode Island WTPs were to switch to monochloramine as a primary disinfectant during water treatment, there would be low risk of exposing consumers to harmful levels of NDMA and other DBPs. Although this particular result is contradictory to traditional NDMA formation potential theory, further studies addressing NDMA reduction with respect to CT would be highly beneficial.

Although the bench-top treatment system was ineffective at removing NDMA precursors, it was highly effective at removing traditional DBP precursors such as TOC and TN. The addition of a GAC column filter proved to reduce levels of TOC and TN by 85% and 86%, respectively. Additions or improvements must be made to the bench-top treatment system to reduce levels of influential NDMA precursors. In future studies, other water treatment practices to consider implementing are membrane filtration, ozone, and UV disinfection. A supplemental fingerprinting study would also prove beneficial for determining the extent of NDMA precursors in Rhode Island and other regional source waters.

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Author Contributions: Maxwell C. Meadows, Soni M. Pradhanang, and Thomas B. Boving conceived and designed the experiments; Maxwell C. Meadows performed the experiments; Takahiro Fujioka and Hitoshi Kodamatani generated

the NDMA data; Maxwell C. Meadows and Soni M. Pradhanang analyzed the data; Maxwell C. Meadows wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Choi, J.; Valentine, R.L. Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloramine: a new disinfection by-product. *Wat. Res.* 2002, 36, 817-824.
doi: 10.1016/S0043-1354(01)00303-7.
2. Mitch, W.A.; Sedlak, D.L. Formation of N-nitrosodimethylamine (NDMA) from dimethylamine during chlorination. *Environ. Sci. Technol.* 2002, 36, 588-595.
doi: 10.1021/es010684q.
3. Choi, J.; Valentine, R.L. N-nitrosodimethylamine formation by free-chlorine-enhanced nitrosation of dimethylamine. *Environ. Sci. Technol.* 2003, 37, 4871-4876.
doi: 10.1021/es034020n.
4. Schreiber, I.M; Mitch, W.A. Nitrosamine formation pathway revisited: the importance of chloramine speciation and dissolved oxygen. *Environ. Sci. Technol.* 2006, 40, 6007-6014.
doi: 10.1021/es060978h.
5. Krasner; S.W. The formation and control of emerging disinfection by-products of health concern. *Phil. Trans. R. Soc. A.* 2009, 367, 4077-4095.
doi: 10.1098/rsta.2009.0108.

6. Nawrocki, J.; Andrzejewski, P. Nitrosamines and water. *J. Haz. Mat.* 2011, 189, 1-18.
doi: 10.1016/j.jhazmat.2011.02.005.
7. Wolff, I.A.; Wasserman, A.E. Nitrates, nitrites, and nitrosamines. *Sci.* 1972, 177, 15-19.
Available online: <http://www.jstor.org/stable/1733909> (accessed on 27-03-2018).
8. Lin, J.K. Nitrosamines as potential environmental carcinogens in man. *Clin. Biochem.* 1990, 23, 67-71.
doi: 10.1016/0009-9120(90)90489-H.
9. Loeppky, R.N. Nitrosamine and N-nitroso compound chemistry and biochemistry. *Am. Chem. Soc.* 1994, 1-18.
doi: 10.1021/bk-1994-0553.ch001.
10. U.S. EPA. Guidelines for carcinogen risk assessment. *Federal Register.* 1986, 22-58.
11. IARC. Evaluation of the carcinogenic risks to humans. *IARC Monographs.* 1987, 7, 1-449.
doi: 10.1002/14356007.a04.

12. A brief history of ndma findings in drinking water. Available online:
http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/NDMAhistory.html (accessed on 27-08-2018).
13. Drinking water standards and guidelines. Available online:
<https://www.mass.gov/guides/drinking-water-standards-and-guidelines>
(accessed on 07-08-2018).
14. Mitch, W.A.; Sedlak, D.L. Characterization and fate of N-nitrosodimethylamine precursors in municipal wastewater treatment plants. *Environ. Sci. Technol.* 2004, 38, 1445-1454.
doi: 10.1021/es035025n.
15. Schreiber, I.M.; Mitch, W.A. Influence of the order of reagent addition on NDMA formation during chloramination. *Environ. Sci. Technol.* 2005, 39, 3811-3818.
doi: 10.1021/es0483286.
16. Kemper, J.M.; Walse, S.S.; Mitch, W.A. Quaternary amines as nitrosamine precursors: a role for consumer products? *Environ. Sci. Technol.* 2010, 44, 1224-1231.
doi: 10.1021/es902840h.

17. Lee, W.; Westerhoff, P.; Croué, J. Dissolved organic nitrogen as a precursor for chloroform, dichloroacetonitrile, N-nitrosodimethylamine, and trichloronitromethane. *Environ. Sci. Technol.* 2007, 41, 5485-5490.
doi: 10.1021/es070411g.
18. Chang, H.; Chen, C.; Wang, G. Identification of potential nitrogenous organic precursors for C-, N-DBPs and characterization of their DBPs formation. *Wat. Res.* 2011, 45, 3753-3764.
doi: 10.1016/j.watres.2011.04.027.
19. Tong, S.T.Y.; Chen, W. Modeling the relationship between land use and surface water quality. *J. Environ. Manag.* 2002, 66, 377-393.
doi: 10.1006/jema.2002.0593.
20. Mitch, W.A.; Gerecke, A.C.; Sedlak, D.L. A N-Nitrosodimethylamine (NDMA) precursor analysis for chlorination of water and wastewater. *Wat. Res.* 2003, 37, 3733-3741.
doi: 10.1016/S0043-1354(03)00289-6.
21. Chen, Z.; Valentine, R.L. Modeling the formation of N-nitrosodimethylamine (NDMA) from the reaction of natural organic matter (NOM) with monochloramine. *Environ. Sci. Technol.* 2006, 40, 7290-7297.
doi: 10.1021/es0605319.

22. Selbes, M.; Beita-Sandí, W.; Kim, D.; Karanfil, T. The role of chloramine species in NDMA formation. *Wat. Res.* 2018, 140, 100-109.
doi: 10.1016/j.watres.2018.04.033.
23. Brisson, I.J.; Levallois, P.; Tremblay, H.; Sérodes, J.; Deblois, C.; Charrois, J.; Taguchi, V.; Boyd, J.; Li, X.; Rodriguez, M.J. Spatial and temporal occurrence of N-nitrosamines in seven drinking water supply systems. *Environ. Monit. Assess.* 2013, 185, 7693-7708.
doi: 10.1007/s10661-013-3128-0.
24. Uzun, H.; Kim, D.; Karanfil, T. Seasonal and temporal patterns of NDMA formation potentials in surface waters. *Wat. Res.* 2015, 69, 162-172.
doi: 10.1016/j.watres.2014.11.017.
25. Bei, E.; Liao, X.; Meng, X.; Li, S.; Wang, J.; Sheng, D.; Chao, M.; Chen, Z.; Zhang, X.; Chen, C. Identification of nitrosamine precursors from urban drainage during storm events: a case study in southern China. *Chemos.* 2016, 160, 323-331.
doi: 10.1016/j.chemosphere.2016.06.081.
26. Vaughan, M.C.H.; Bowden, W.B.; Shanley, J.B.; Vermilyea, A.; Sleeper, R.; Gold, A.J.; Pradhanang, S.M.; Inamdar, S.P.; Levia, D.F.; Andres, A.S.; Birgand, F.; Schroth, A.W. High-frequency dissolved organic carbon and nitrate measurements reveal differences in storm hysteresis and loading in

- relation to land cover and seasonality. *Wat. Resour. Res.* 2017, 53, 5345-5363.
- doi: 10.1002/2017WR020491.
27. Stevens, A.A; Moore, L.A.; Miltner, R.J. Formation and control of non-trihalomethane disinfection by-products. *J. AWWA.* 1989, 81, 54-60.
- Available online: <https://www.jstor.org/stable/41292790> (accessed on 23-06-2019).
28. AWWA. Water chlorination/ chloramination practices and principles. *AWWA Manual*, 2006, 2, 1-188.
29. Bond, T.; Goslan, E.H.; Parsons, S.A.; Jefferson, B. A critical review of trihalomethane and haloacetic acid formation from natural organic matter surrogates. *Environ. Technol. Rev.* 2012, 1, 93-113.
- doi: 10.1080/09593330.2012.705895.
30. Community water treatment. Available online: https://www.cdc.gov/healthywater/drinking/public/water_treatment.html (accessed on 23-06-2019).
31. Hanigan, D.; Zhang, J.; Herckes, P.; Krasner, S.W.; Chen, C.; Westerhoff, P. Adsorption of N-nitrosodimethylamine precursors by powdered and granular activated carbon. *Environ. Sci. Technol.* 2012, 46, 12630-12639.
- doi: 10.1021/es302922w.

32. Leavey-Roback, S.L.; Sugar, C.A.; Krasner, S.W.; Suffet, I.H. NDMA formation during drinking water treatment: A multivariate analysis of factors influencing formation. *Wat. Res.* 2016, 95, 300-309.
doi: 10.1016/j.watres.2016.02.060.
33. Frazar, S.; Gold, A.J.; Addy, K.; Moatar, F.; Birgand, F.; Schroth, A.; Kellogg, D.Q. Contrasting behavior of nitrate and phosphate flux from high flow events on small agricultural and urban watersheds. *Biogeochem* (under review).
34. Chambers, B.M.; Pradhanang, S.M.; Gold, A.J. Simulating climate change induced thermal stress in coldwater fish habitat using SWAT model. *Water*. 2017, 9, 1-24.
doi: 10.3390/w9100732.
35. Climate information. Available online: <https://www.ncdc.noaa.gov/climate-information> (accessed on 24-06-2019).
36. Silva, M.K.; Wada, T.K.; Study of the formation of stable high concentrated monochloramine solutions. *Sys. Eng.* 2016, 1-9.
37. Kodamatani, H.; Yamazaki, S.; Saito, K.; Amponsaa-Karikari, A.; Kishikawa, N.; Kuroda, N.; Tomiyasu, T.; Komatsu, Y. Highly sensitive method for determination of N-nitrosamines using high-performance liquid

- chromatography with online UV irradiation and luminol chemiluminescence detection. *J. Chromatogr. A.* 2009, 1216, 92-98.
doi: 10.1016/j.chroma.2008.11.025.
38. Kodamatani, H.; Roback, S.L.; Plumlee, M.H.; Ishida, K.P.; Masunaga, H.; Maruyama, N.; Fujioka, T. An inline ion-exchange system in a chemiluminescence-based analyzer for direct analysis of N-Nitrosamines in treated wastewater. *J. Chromatogr. A.* 2018, 1553, 51-56.
doi: 10.1016/j.chroma.2018.04.030.
39. Fujioka, T.; Takeuchi, H.; Tanaka, H.; Nghiem, L.D.; Ishida, K.P.; Kodamatani, H. A rapid and reliable technique for N-nitrosodimethylamine analysis in reclaimed water by HPLC-photochemical reaction-chemiluminescence. *Chemos.* 2016, 161, 104-111.
doi: 10.1016/j.chemosphere.2016.06.094.
40. Gerecke, A.C.; Sedlak, D.L. Precursors of N-nitrosodimethylamine in natural waters. *Environ. Sci. Technol.* 2003, 37, 1331-1336.
doi: 10.1021/es026070i.
41. West, D.M.; Wu, Q.; Donovan, A.; Shi, H.; Ma, Y.; Jiang, H.; Wang, J. N-nitrosamine formation by monochloramine, free chlorine, and peracetic acid disinfection with presence of amine precursors in drinking water system. *Chemos.* 2016, 153, 521-527.

doi: 10.1016/j.chemosphere.2016.03.035.

42. Najm, I.; Trussell, R. NDMA formation in water and wastewater. *J. AWWA*. 2001, 93, 92-99.

doi: 10.1002/j.1551-8833.2001.tb09129.x.
43. Charrois, J.W.A.; Boyd, J.M.; Froese, K.L.; Hruddy, S.E. Occurrence of N-nitrosamines in Alberta public drinking-water distribution systems. *J. Environ. Eng. Sci.* 2007, 6, 103-114.

doi: 10.1139/s06-031.
44. Zhao, Y.; Boyd, J.M.; Woodbeck, M.; Andrews, R.C.; Qin, F.; Hruddy, S.E.; Li, X. Formation of N-nitrosamines from eleven disinfection treatments of seven different surface waters. *Environ. Sci. Technol.* 2008, 42, 4857-4862.

doi: 10.1021/es7031423.
45. Farré, M.J.; Jaén-Gil, A.; Hawkes, J.; Petrovic, M.; Catalán, N. Orbitrap molecular fingerprint of dissolved organic matter in natural waters and its relationship with NDMA formation potential. *Sci. Tot. Environ.* 2019, 670, 1019-1027.

doi: 10.1016/j.scitotenv.2019.03.280.
46. Inamdar, S.; Finger, N.; Singh, S.; Mitchell, M.; Levia, D.; Bais, H.; Scott, D.; McHale, P. Dissolved organic matter (DOM) concentration and quality in a forested mid-Atlantic watershed, USA. *Biogeochem.* 2012, 108, 55-76.

doi: 10.1007/s10533-011-9572-4.

47. Yoon, B.; Raymond, P.A. Dissolved organic matter export from a forested watershed during Hurricane Irene. *Geophys. Res. Let.* 2012, 39, 1-6.
doi: 10.1029/2012GL052785.
48. Singh, S.; Inamdar, S.; Mitchell, M.; McHale, P. Seasonal pattern of dissolved organic matter (DOM) in watershed sources: Influence of hydrologic flow paths and autumn leaf fall. *Biogeochem.* 2014, 118, 321-337.
doi: 10.1007/s10533-013-9934-1.
49. Duan, S.; Delaney-Newcomb, K.; Kaushal, S.S.; Findlay, S.E.G.; Belt, K.T. Potential effects of leaf litter on water quality in urban watersheds. *Biogeochem.* 2014, 121, 61-80.
doi: 10.1007/s10533-014-0016-9.
50. Lusk, M.G.; Toor, G. Dissolved organic nitrogen in urban streams: biodegradability and molecular composition studies. *Wat. Res.* 2016, 96, 225-235.
doi: 10.1016/j.watres.2016.03.060.
51. Chiang, P.C.; Chang, E.E.; Liang, C.H. NOM characteristics and treatabilities of ozonation processes. *Chemos.* 2002, 46, 929-936.
doi: 10.1016/S0045-6535(01)00181-3.

52. Chen, C.; Zhang, X.; Zhu, L.; He, W.; Han, H. Changes in different organic matter fractions during conventional treatment and advanced treatment. *J. Environ. Sci.* 2011, 23, 582-586.
53. Qualls, R.G.; Haines, B.L. Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem. *Soil. Sci. Soc. America. J.* 1991, 55, 1112-1123.
54. Yu, Z.; Zhang, Q.; Kraus, T.E.C.; Dahlgren, R.A.; Anastasio, C.; Zasoski, R.J. Contribution of amino compounds to dissolved organic nitrogen in forest soils. *Biogeochem*, 2002, 61, 173-198.
doi: 10.1023/A:1020221528515.
55. U.S. EPA. Finished water storage facilities. 2002

APPENDICES

CHAPTER 2



Fig. A1. Magnified view of NDMA (2 $\mu\text{g/L}$). The peak at 11.75 min was identified as benzene.



Fig. A2. Magnified view of NMEA (2 $\mu\text{g/L}$). Very low peak signal suggests 2 $\mu\text{g/L}$ is possible MDL for this target analyte.

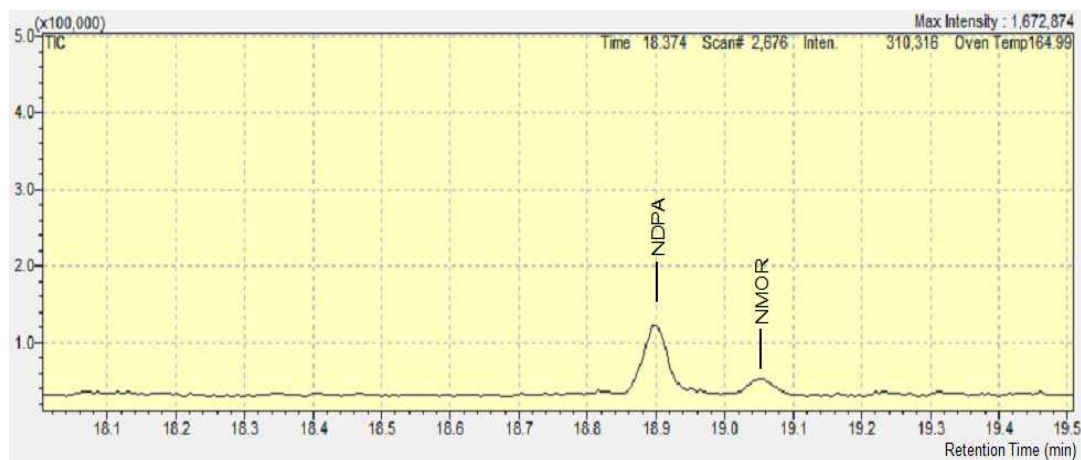


Fig. A3. Magnified view of NDPA and NMOR (2 $\mu\text{g/L}$). Low NMOR peak signal suggests 2 $\mu\text{g/L}$ is possible LOD for this target analyte.



Fig. A4. Magnified view of NPIP (2 $\mu\text{g/L}$). The peak at 20.36 min was identified as a hydrocarbon.



Fig A.5. Magnified view of NDBA (2 µg/L).

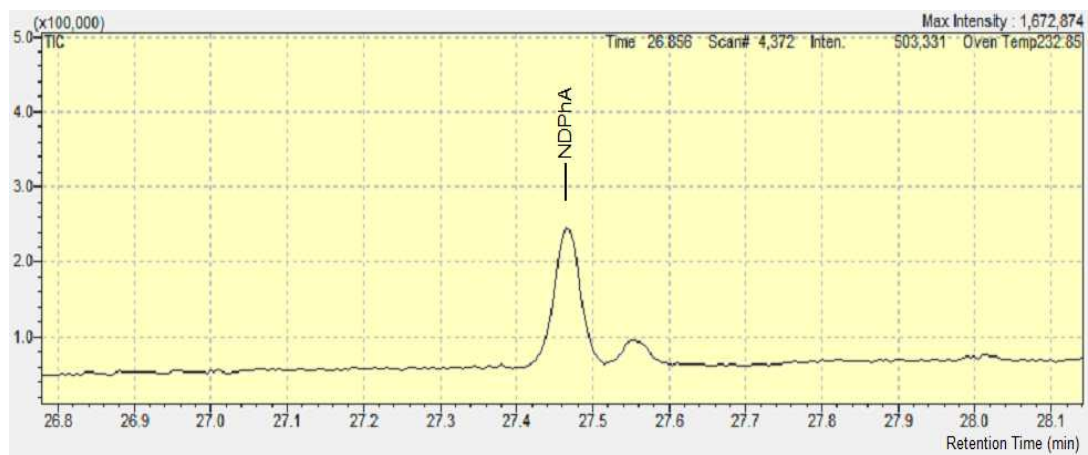


Fig A.6. Magnified view of NDPhA (2 µg/L).

CHAPTER 3

Table A1 ANOVA table comparing the main and interaction effects of treatment

(R, F, GAC), season, and CT on the formation of NDMA at Bailey Brook.

	DF	Sum of Squares	Mean Square	F Value	P Value
Treatment	2	2.3904	1.1952	2.8425	0.0846
CT	1	6.7687	6.7687	16.0977	0.0008
Season	2	3.4009	1.7004	4.0441	0.0354
Treatment * CT	2	2.0068	1.0034	2.3864	0.1204
Treatment * Season	4	3.4209	0.8552	2.0340	0.1325
CT * Season	2	4.5208	2.2604	5.3759	0.0148
Treatment * CT * Season	4	2.7345	0.6836	1.6259	0.2111
Model	17	25.2430	1.4849	3.5314	0.0055
Error	18	7.5686	0.4205	0.0000	0.0000
Corrected Total	35	32.8116	0.0000	0.0000	0.0000

Table A2. ANOVA table comparing the main and interaction effects of treatment

(R, F, GAC), season, and CT on the formation of NDMA at Cork Brook.

	DF	Sum of Squares	Mean Square	F Value	P Value
Treatment	2	2.4361	1.2181	0.5233	0.6013
CT	1	590.5710	590.5710	253.7050	0.0000
Season	2	16.9428	8.4714	3.6393	0.0471
Treatment * CT	2	5.0976	2.5488	1.0950	0.3558
Treatment * Season	4	6.5504	1.6376	0.7035	0.5998
CT * Season	2	6.9425	3.4713	1.4912	0.2516
Treatment * CT * Season	4	1.0857	0.2714	0.1166	0.9749
Model	17	629.6261	37.0368	15.9108	0.0000
Error	18	41.9002	2.3278	0.0000	0.0000
Corrected Total	35	671.5263	0.0000	0.0000	0.0000

Table A3. ANOVA table comparing the main and interaction effects of treatment

(R, F, GAC), season, and site on TN concentration.

	DF	Sum of Squares	Mean Square	F Value	P Value
Treatment	2	3.9305	1.9652	876.6803	0.0000
Season	2	0.4681	0.2341	104.4126	0.0000
Site	1	1.2137	1.2137	541.4139	0.0000
Treatment * Season	4	0.2418	0.0605	26.9703	0.0000
Treatment * Site	2	0.8144	0.4072	181.6444	0.0000
Season * Site	2	0.8517	0.4259	189.9789	0.0000
Treatment * Season * Site	4	0.4459	0.1115	49.7336	0.0000
Model	17	7.9661	0.4686	209.0389	0.0000
Error	18	0.0404	0.0022	0.0000	0.0000
Corrected Total	35	8.0065	0.0000	0.0000	0.0000

Table A4. ANOVA table comparing the main and interaction effects of treatment

(R, F, GAC), season, and site on NPOC concentration.

	DF	Sum of Squares	Mean Square	F Value	P Value
Treatment	2	301.9348	150.9674	913.9232	0.0000
Season	2	367.4674	183.7337	1112.2829	0.0000
Site	1	1.4280	1.4280	8.6450	0.0088
Treatment * Season	4	133.9149	33.4787	202.6727	0.0000
Treatment * Site	2	1.6435	0.8217	4.9746	0.0191
Season * Site	2	41.2818	20.6409	124.9554	0.0000
Treatment * Season * Site	4	10.3619	2.5905	15.6822	0.0000
Model	17	858.0323	50.4725	305.5492	0.0000
Error	18	2.9734	0.1652	0.0000	0.0000
Corrected Total	35	861.0056	0.0000	0.0000	0.0000

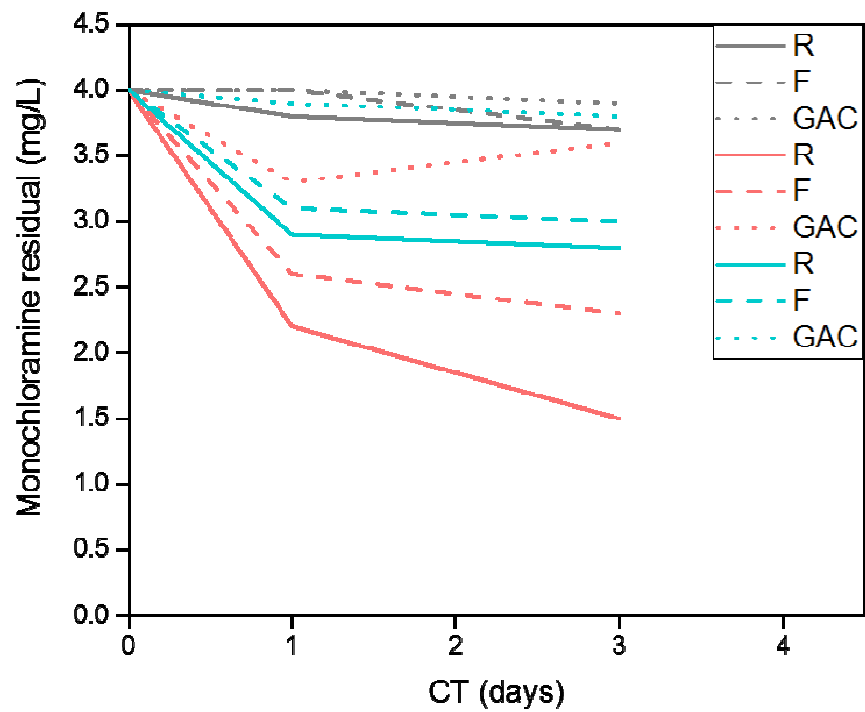


Figure A7. Residual monochloramine measurements in Bailey Brook samples.

Summer samples are identified by gray lines, Fall samples are identified by red lines, Spring samples are identified by blue lines.

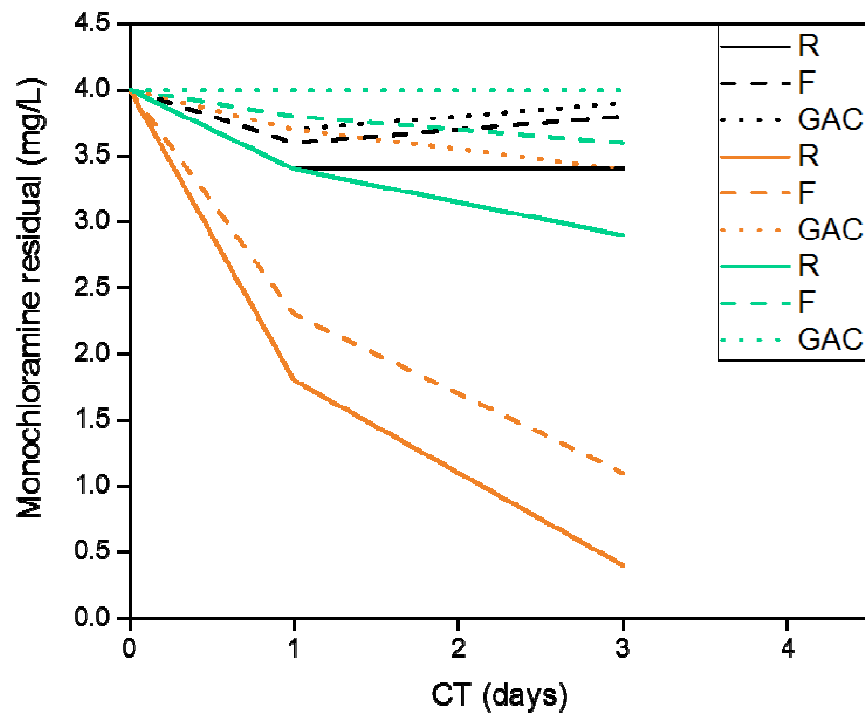


Figure A8. Residual monochloramine measurements in Cork Brook samples.

Summer samples are identified by black lines, Fall samples are identified by orange lines, Spring samples are identified by green lines.